NMR KNIGHT SHIFTS AND LINEWIDTHS IN THE Ni-Pd-P AND Ni-Pt-P METALLIC GLASSES: COMPOSITION AND TEMPERATURE DEPENDENCES*

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ABSTRACT

NMR Knight shift and linewidth measurements are reported for the ^{31}P nuclei in the metallic glasses $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ (where x = 16 to 26.5) and $(Ni_yPd_{1-y})_{80}P_{20}$ (where y = 0.20 to 0.80), and both the ^{31}P and ^{195}Pt nuclei in the metallic glass $(Ni_yPt_{1-y})_{75}P_{25}$ (where y = 0.20 to 0.68). The results are discussed in terms of the amorphous structure, electronic structure, and stability of transition metal + metalloid metallic glasses.

I. INTRODUCTION

Recently, considerable attention has been focused on a class of materials known as metallic glasses [1]. This is due both to a desire for a re-examination of some heretofore fundamental concepts of solids as well as a possibility for a variety of technological applications. Metallic glasses have the general form $TM_{100-x}M_x$, where TM is a transition metal (or combination of transition metals) such as Fe, Ni, Pd or Pt and M is a high valence metalloid such as B, C, Si or P. For the most part, such alloys are prepared by rapid quenching from the liquid state and possess compositions typically ranging from x = 15 to 28 at. % for the metalloid.

This work describes the application of nuclear magnetic resonance (NMR) in the study of the Ni-Pt-P and Ni-Pd-P metallic glass systems. In particular, we have exploited the NMR Knight shift to gain information about electrons at or near the Fermi Energy. Spectra obtained from both the transition metal and metalloid elements shed light on the: (1) amorphous structure, (2) electronic structure and (3) bonding and stability. This in turn leads to a better understanding of the electronic, magnetic and mechanical properties for metallic glasses.

II. EXPERIMENTAL PROCEDURE

NMR Knight shift and linewidth measurements are presented for the ^{31}P nuclei in the metallic glass systems $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ (where x = 16, 17, 20, 23, 25 and 26.5) and $(Ni_yPd_{1-y})_{80}P_{20}$ (where y = 0.20, 0.30, 0.40, 0.50, 0.60, 0.70 and 0.80), and both the ^{31}P and ^{195}Pt nuclei in the metallic system $(Ni_yPt_{1-y})_{75}P_{25}$ (where y = 0.20, 0.30, 0.40, 0.50, 0.60, 0.64 and 0.68). All of the alloys were prepared by a rapid quenching process (piston and anvil technique) described in detail elsewhere [2]. The foils which resulted from this process were about 50 μm thick and 2.5 cm in diameter, and were checked by x-ray diffraction to verify their glassy structure.

The NMR measurements were carried out between 77 °K and room temperature, for frequencies from 4 to 16 MHz, by utilizing a Varian wideline VF-16 cross coil spectrometer with the related cryogenic accessories. Spectra were obtained from the ^{31}P nuclei in all the samples and ^{195}Pt nuclei in $(Ni_{0.20}Pt_{0.80})_{75}P_{25}$ only by sweeping the dc field with fixed frequency. The field was calibrated with ^7Li ions in solution. Typical NMR spectra (derivatives of the absorption curves) for the ^{31}P and ^{195}Pt resonances have been illustrated in an earlier paper [3]. It was noted that the lineshapes for ^{31}P demonstrated some asymmetry in that the low field side was broader. The ^{195}Pt resonance was quite broad and possessed a great deal of intensity in the tails. Some preliminary Knight shift and linewidth measurements have been reported earlier [3,4].

III. RESULTS AND ANALYSIS

A. NMR Knight Shift

Figure 1 shows the observed room temperature ^{31}P Knight shift (in %), K, (defined by the derivative crossover point) as a function of P concentration, x, for the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ system. Data are shown for a resonance frequency, ν, of 8 MHz. It can be seen that the Knight shift demonstrates a strong decrease as the P concentration increases from x = 16 to 26.5. The dependence is essentially linear and extrapolates to zero Knight shift for x = 40. The variation of the ^{31}P Knight shift with frequency for the respective $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ compositions is shown in Figure 2 (closed symbols and dashed lines). It can be seen that all six compositions studied have no detectable frequency dependence within the error. For comparison, the ^{31}P Knight shift frequency dependences for the $(Ni_yPd_{1-y})_{80}P_{20}$ and $(Ni_yPt_{1-y})_{75}P_{25}$ systems to be discussed below are included (vertical lines with bars); again, no variation with frequency is observed.

Figures 3 and 4 show the observed room temperature ^{31}P Knight shift as a function of Ni concentration, y, for $(Ni_yPd_{1-y})_{80}P_{20}$ and $(Ni_yPt_{1-y})_{75}P_{25}$ respectively. For both systems, the data shown were obtained at 8 MHz. In contrast to the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ results, both $(Ni_yPd_{1-y})_{80}P_{20}$ and $(Ni_yPt_{1-y})_{75}P_{25}$ have a Knight shift which remains unchanged within the error over the entire range of Ni concentration (y = 0.20 to 0.80 in the former and y = 0.20 to 0.68 in the latter). This behavior might be expected as a change in P concentration would vary the average number of electrons per atom while a change in Ni relative to Pd or Ni relative to Pt would not. As indicated above, and in Figure 2, there is no frequency dependence of the ^{31}P Knight shift for these systems. The solid vertical lines with bars, at the various frequencies represent the range of shift values for the seven compositions of $(Ni_yPd_{1-y})_{80}P_{20}$ and seven compositions of $(Ni_yPt_{1-y})_{75}P_{25}$. The slight frequency dependences reported earlier were due to very small discrepancies in the NMR standards used to mark field [4]. It is important to note that the shift value characteristic of all the $(Ni_yPd_{1-y})_{80}P_{20}$ alloys is the same as that for $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ with x = 20. Similarly, the

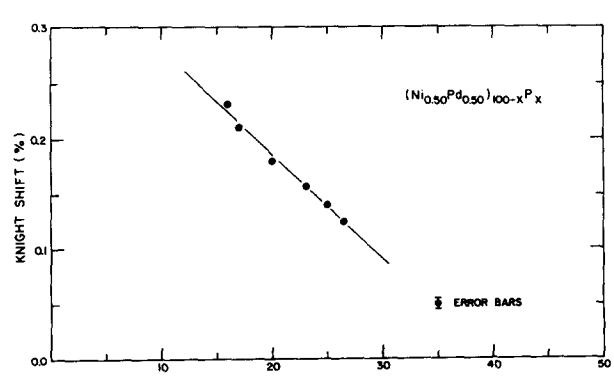

Fig. 1. Room temperature ^{31}P Knight shift (in %) versus P concentration for the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ alloys: ν = 8 MHz.

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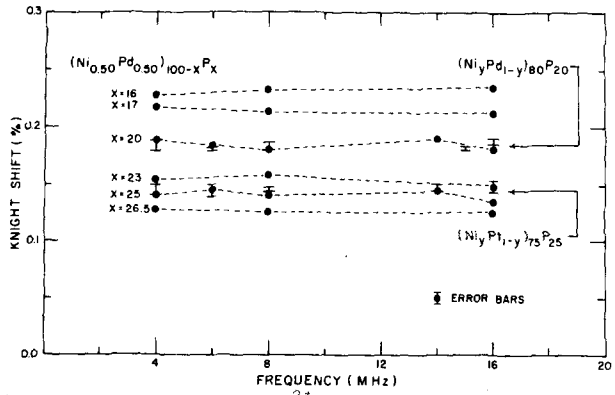

Fig. 2. Room temperature ^{31}P Knight shift (in %) versus resonance frequency (in MHz) for the various $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ alloys; vertical lines with bars represent $(Ni_yPd_{1-y})_{80}P_{20}$ and $(Ni_yPt_{1-y})_{75}P_{25}$.

value characteristic of all the $(Ni_yPt_{1-y})_{75}P_{25}$ alloys is the same as that for $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ with $x = 25$. Consequently, a certain degree of similarity in the electronic structure for the three systems is expected. The ^{31}P Knight shift for all the alloys increased essentially linearly by 0.010% between 77 °K and room temperature.

The ^{195}Pt resonance was observed in the $(Ni_{0.20}Pt_{0.80})_{75}P_{25}$ sample at 77 °K and room temperature. The resonance spectrum is quite broad with a linewidth of about 40 Oe and possessing a great deal of intensity in the tails. The most striking feature of the ^{195}Pt resonance in the metallic glass is a room temperature Knight shift value, corresponding to the derivative crossover point, of approximately $-0.1\% \pm 0.05\%$. There was no detectable temperature dependence for the ^{195}Pt Knight shift, although with the broad line, we can only state that any change in shift between 77 °K and room temperature is less than 0.05%. This is to be compared with a value of -3.5% for ^{195}Pt in pure crystalline Pt. The large negative Knight shift for ^{195}Pt in Pt metal has been attributed to a dominant core polarization contribution and the resulting positive increase in the Knight shift for ^{195}Pt in the metallic glass provides strong evidence that the TM d-states are filled which is consistent with a charge transfer from the metalloid to transition metal atoms. A calculation of the resonance intensity and an investigation of the saturation behavior verify that the ^{195}Pt resonance is indeed characteristic of Pt in the metallic glass and not a small amount of Pt which has formed a second phase or non-metallic phase. Furthermore, the wide linewidth for the ^{195}Pt resonance suggests a broad distribution in the degree of the d-state filling.

B. NMR Linewidth

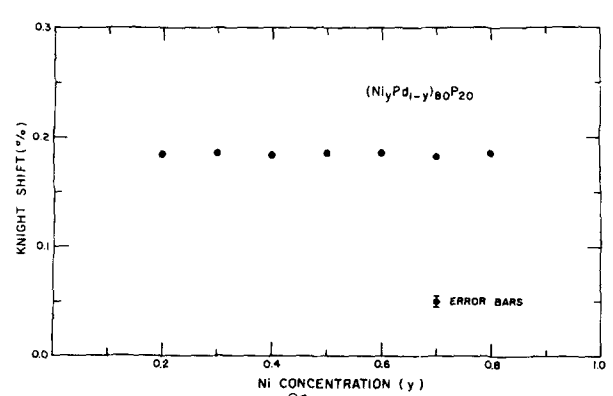

Fig. 3. Room temperature ^{31}P Knight shift (in %) versus Ni concentration for the $(Ni_yPd_{1-y})_{80}P_{20}$ alloys: $\nu = 8$ MHz.

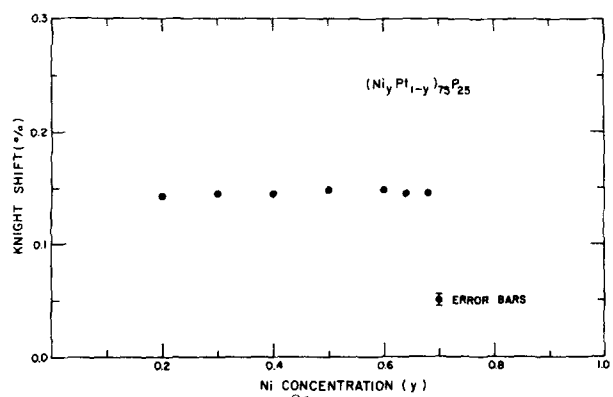

Fig. 4. Room temperature ^{31}P Knight shift (in %) versus Ni concentration for the $(Ni_yPt_{1-y})_{75}P_{25}$ alloys: $\nu = 8$ MHz.

The room temperature NMR (peak-to-peak) linewidth, δ, for the ^{31}P resonance has been measured for all compositions with resonance frequencies ranging from $\nu = 4$ to 16 MHz. For every composition, the linewidth increases continuously with frequency in a manner which is indicative of a broadening mechanism resulting from a distribution of Knight shifts. As pointed out in reference 3, this is a consequence of the P atoms having a variety of environments in the glassy structure. The ^{31}P linewidth data for all of the alloys can be fitted extremely well by the form

$$\delta = [(\delta_1)^2 + (\delta_2)^2]^{1/2}, \qquad (1)$$

where $\delta_1 = c\nu$ is the frequency dependent contribution and δ_2 represents the frequency independent contribution (e.g. dipolar broadening). Such a form is appropriate for combining uncorrelated broadening mechanisms. The values obtained for c and δ_2 associated with the various compositions of $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$, $(Ni_yPd_{1-y})_{80}P_{20}$ and $(Ni_yPt_{1-y})_{75}P_{25}$ are listed in Tables I, II and III respectively.

Due to signal-to-noise problems arising from a poor filling factor, the ^{195}Pt linewidth could only be measured in the $(Ni_{0.20}Pt_{0.80})_{75}P_{25}$ sample at 8 MHz. As indicated above, the peak-to-peak width was approximately 40 Oe.

The linewidth for ^{31}P in all the alloys and ^{195}Pt in $(Ni_{0.20}Pt_{0.80})_{75}P_{25}$ remained unchanged as the temperature was varied between 77 °K and room temperature.

IV. DISCUSSIONS AND CONCLUSIONS

A. Electronic Structure (Density of States)

For all three systems, we attribute the ^{31}P Knight shift to two principal contributions, i.e. $K = K_s + K_d$, where K_s is the "direct contact shift" resulting from a polarization of the conduction s-electrons by the external magnetic field which is communicated to the ^{31}P nuclei via a contact hyperfine interaction and K_d is the "d polarization shift" resulting from a polarization of the transition metal d-electrons by the extermal magnetic field which is communicated to the ^{31}P nuclei via a s-d interaction that polarizes the conduction s-electrons (together with the contact hyperfine

TABLE I

x	c (Oe/MHz)	δ_2 (Oe)
16	0.75	1.7
17	0.65	1.4
20	0.46	1.4
23	0.37	1.4
25	0.34	1.4
26.5	0.31	1.4

Values of c and δ_2 obtained by fitting the linewidth data for $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ alloys to eqn. (1).

TABLE II

y	c (Oe/MHz)	δ_2 (Oe)
0.20	0.42	1.3
0.30	0.46	1.1
0.40	0.45	1.2
0.50	0.46	1.4
0.60	0.48	1.4
0.70	0.51	0.9
0.80	0.56	0.9

Values of c and δ_2 obtained by fitting the linewidth data for $(Ni_yPd_{1-y})_{80}P_{20}$ alloys to eqn. (1).

interaction). Using the customary two-band model, we can relate the two shift contributions to corresponding terms in the bulk magnetic susceptibility, χ, and density of states, N(E), by

$$K = \alpha_s\chi_s + \alpha_d\chi_d = \alpha_s\mu_B^2 N_s(E_F) + \alpha_d\mu_B^2 N_d(E_F), \qquad (2)$$

where χ_s and χ_d are the paramagnetic spin susceptibilities, α_s and α_d are the coupling coefficients of the electron-nucleus interactions, and $N_s(E_F)$ and $N_d(E_F)$ are the density of states at the Fermi energy for the s- and d-bands respectively. In a simple rigid band picture, a variation of the P concentration, x, in the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ system changes the electron concentration and shifts the Fermi energy. Consequently, the Knight shift measurements map out a portion of the density of states. Preliminary measurements of the magnetic susceptibility are consistent with this description. We attribute the strong decrease in K as x increases to a filling up of the transition metal d-states because of a charge transfer from the P metalloid atoms. As indicated above, the observation of the ^{195}Pt resonance in $(Ni_{0.20}Pt_{0.80})_{75}P_{25}$ provides additional evidence for the existence of charge transfer.

A change in temperature will also shift the Fermi energy and $N(E_F)$. However, an analysis of the magnitude and sign of the temperature dependence for all of our ^{31}P Knight shifts indicates that simple thermal expansion effects are dominant.

B. Amorphous Structure

Of all the models proposed for the amorphous structure of metallic glasses, the one suggested by Polk seems particularly promising [5]. In Polk's model, a dense random packing (DRP) structure is postulated for the transition metal atoms with the metalloid atoms occupying the larger (interstitial) holes. Some preliminary NMR linewidth data has already been discussed in the context of the Polk model [3].

As indicated in Section III, part B, all three systems exhibit a frequency dependent ^{31}P linewidth which is indicative of a broadening mechanism resulting from a distribution of Knight shifts. This is a consequence of the P atoms having a variety of environments in the glassy structure and, correspondingly, a distribution in the degree of transition metal d-state filling results. The distribution in Knight shifts enters through the K_d term.

For the $(Ni_yPt_{1-y})_{75}P_{25}$ alloys (P concentration fixed), we note that the linewidth c value remains constant for $0.20 \leq y \leq 0.50$ and then decreases continuously for $0.50 < y \leq 0.68$ (see Table III). This behavior indicates that the distribution in Knight shifts, and correspondingly, the distribution in P sites is reduced for $y > 0.50$. The situation is reversed for the $(Ni_yPd_{1-y})_{80}P_{20}$ alloys (P concentration fixed) in that the c value remains essentially constant for $0.20 \leq y \leq 0.50$ and then increases continuously for $0.50 < y \leq 0.80$ (see Table II). In this system, the distribution in P sites is increased for $y > 0.50$ although the increase is not as pronounced as the observed decrease for the $(Ni_yPt_{1-y})_{75}P_{25}$ alloys. The behavior observed for these two systems could result from a "phasing out" or "phasing in" of P sites above a particular concentration ($y = 0.50$). In particular, a tendency for "phase separation" has been suggested for the $(Ni_yPt_{1-y})_{75}P_{25}$ system [6]. The behavior could also result from variations in the DRP structure caused by atomic size effects. In the $(Ni_yPd_{1-y})_{80}P_{20}$ system, the difference in size between Ni and Pd is important [6]. For the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ alloys (P concentration varies), the strong decrease in Knight shift with x is followed by a similar decrease in c value.

TABLE III

y	c (Oe/MHz)	δ_2 (Oe)
0.20	0.40	2.0
0.30	0.40	1.9
0.40	0.40	1.8
0.50	0.40	1.8
0.60	0.35	1.4
0.64	0.31	1.4
0.68	0.28	1.3

Values of c and δ_2 obtained by fitting the linewidth data for $(Ni_yPt_{1-y})_{75}P_{25}$ alloys to eqn. (1).

C. Bonding and Stability

Three microscopic descriptions for the nature of the bonding and stability in metallic glasses have been advanced. The first, based on the DRP structure described above, suggests that the transfer of charge from the metalloid to the transition metal atoms results in a form of ionic-like bonding which stabilizes the structure [5]. The second suggests that a chemical (covalent-like) bonding stabilizes the structure [7]. The third, based on the nearly free electron (NFE) approach, suggests that the alloy is most stable when the composition is such that the Fermi level lies at a minimum in the density of states [8]. As indicated above in Section IV, part A, the ^{31}P and ^{195}Pt Knight shift results provide strong evidence for the idea of a charge transfer from the metalloid to the transition metal atoms. In addition, the measurements show no evidence of any minimum in the density of states as required by the NFE model. X-ray photoemission experiments on the metallic glass $Pd_{77.5}Cu_{6.0}Si_{16.5}$ are inconsistent with the existence of chemical bonding, however, these results have been questioned recently and the matter remains unresolved [9].

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*Work at University of Connecticut supported in part by the University of Connecticut Research Foundation and at California Institute of Technology by the U. S. Energy Research and Development Administration under Contract No. AT(04-3)-822.

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